

# Inorganic pre-polymerized coagulants: current status and future trends

A.I. ZOUBOULIS\*, N.D. TZOUPANOS and P.A. MOUSSAS

Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki  
GR-54124, GREECE  
tel: +302310997794

**Abstract:** The aim of this paper is to provide an overview of the evolution of inorganic pre-polymerized coagulants by summarizing the latest developments in their composition and properties. Considerable attention has been paid in recent years to preparing pre-polymerized metal-ion coagulants, based on either aluminium (e.g. polyaluminium chloride, PAC), or ferric ion (e.g. polyferric sulphate, PFS), as they exhibit a better performance than the conventional coagulants (aluminium or iron (III) based salts). However, their efficiency is still much lower than the organic polymeric coagulants. Therefore, attempts have been made to improve further the efficiency of pre-polymerized coagulants either by producing a mixed coagulant (containing both aluminium and iron), or by adding other components to produce new composite coagulants. Concerning the second approach, the additive most frequently used is the polysilicic acid, while it is suggested but yet not well established that organic compounds (e.g. polydimethyldiallylammonium chloride, PDMDAAC) may also be employed for such a purpose. Finally, the modified inorganic pre-polymerised coagulants were found to exhibit a better coagulation performance in treating water and wastewater, when compared with the non-modified ones.

**Key-Words:** Coagulation; flocculation; inorganic pre-polymerized coagulants; modified inorganic coagulants; polyaluminium silicate chloride; polyferric silicate sulfate.

## 1. Introduction

Drinking water of high quality is essential for human beings. Drinking water quality is evaluated by means of certain physical, chemical and biological parameters and consequently, limiting values has been set in accordance to national or international regulations. The natural surface waters are usually polluted from the air and soil by organic or inorganic impurities, which can be either in dissolved, or in particulate form. Inorganic particulates, consisting of clay, mineral oxides and silt, typically enter surface waters by natural erosion processes. On the other hand, organic constituents consisting from viruses, bacteria, algae, protozoan cysts etc can be found in particulate form. Additionally, surface waters usually contain colloidal and dissolved organic substances, such as humic or fulvic acids, arising from the decay of organic debris. Particulate and dissolved organic matter is often identified by the term Natural Organic Matter (NOM) [1]. Most of the impurities found in natural waters, lie in the colloidal size range (i.e. <1  $\mu\text{m}$ ) and are negatively charged; hence, the colloidal dispersion is stable, due to electrostatic repulsive forces, which normally overwhelm the attractive van-der-Waals forces [2]. The removal of such contaminants is essential, as their presence deteriorates the water quality by: (a) reducing the clarity of water (turbidity, colour), (b) causing infection, and (c)

carrying toxic compounds, adsorbed on their surfaces. In addition, NOM is the main precursor to the formation of disinfection byproducts, when chlorine is applied as disinfection agent.

To comply with drinking water standards, water treatment plants remove these impurities by sedimentation and/or filtration, following the processing of water by coagulation/flocculation. The coagulation process by the addition of hydrolyzing inorganic chemicals (coagulants) can involve: 1) the destabilisation of suspended and colloidal particulate matter, 2) the adsorption of portions of colloidal and dissolved NOM onto the surface of the destabilised particles, and 3) the aggregation of the destabilised particles and the subsequent creation of flocs, which enmesh suspended, colloidal and dissolved material as they settle [1].

Typically chemicals (coagulation reagents) used for water (and/or wastewater treatment) are predominantly inorganic salts of Al or Fe, such as  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{FeCl}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$  etc. The coagulation process, when using inorganic Al/Fe salts, can take place under two major mechanisms: a) charge neutralization, and b) sweep coagulation, with respect to the coagulant dosages and to the pH of treated water. Under the charge neutralization mechanism, the active hydrolysis species of Al/Fe with high cationic charge can be strongly adsorbed onto the negatively

charged surfaces of the particles, or on dissolved NOM, thus reducing their charge, minimizing the repulsive forces and eventually causing precipitation and particle aggregation, due to stronger van der Waals attraction. In general, the charge neutralization mechanism is favored in low pH (<6) and low ionic strength waters and additionally, it requires lower coagulant dosages and produces less sludge in comparison with the sweep coagulation mechanism [3].

When Al/Fe salts are used at concentrations exceeding those required for the formation of amorphous metal hydroxide solids, particulate matter and dissolved organic species become entrapped in the amorphous precipitate as they form and settle. This phenomenon is described as "sweep coagulation". This mechanism applies in water treatment applications, where pH values are generally maintained between 6 and 8 and coagulants dosages exceed saturation, with respect to the concentration needed for the formation of amorphous hydroxides [1]. In the sweep coagulation mechanism the optimal coagulant dosage and pH value are not as important parameters, as in the case of charge neutralization. The major drawback of such mechanism is the significantly higher coagulant dosages applied and the production of more sludge, when compared to that of charge neutralization.

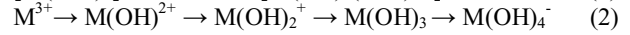
## 2. Inorganic Polymeric Flocculants (IPFs)

The increasing demand of more efficient coagulation treatment, especially regarding the removal of NOM, has led to the development of a new category of coagulants, the Inorganic Polymeric Flocculants (IPFs). Their properties were intensively examined and it has been proved that they are more efficient in lower dosages, for the removal of natural organic matter (NOM), in greater pH, temperature and colloids concentration range than the conventional non-polymerized ones, resulting in more cost-effective treatment [1]. The research efforts have focused during the last two decades on studying the properties and aquatic behavior of these coagulants and it is now well understood that their superiority is related to the different metal species distribution in the polymerized, as compared with the non-polymerized solutions [4, 5].

### 2.1 Aquatic behavior of metal (Al/Fe) salts

Aluminium and iron exist in water solutions (at pH<3) as six coordinated  $Al^{3+}$  and  $Fe^{3+}$  ions respectively, which are the initial monomeric hydrolysis products. As the hydrolysis proceeds,

described by the generic equation (1), various hydrolysis products can be formed. Equation (2) describes the different monomeric products of metal hydrolysis.



Each step in eq. (2) involves displacement of a proton with a hydroxyl ion, while an increase of pH value shifts the equilibrium from left to right. In Fig. 1, the distribution of Fe/Al species regarding to pH variation is presented [2]. The pH value designates the metal species present, and affects the efficiency of coagulants, i.e. in the case of conventional coagulants, the pH range, at which the precipitate  $M(OH)_3$  is formed, is critical, as the sweep coagulation is considered as the major coagulation mechanism.

The equation (2) is a simplified description of the hydrolysis process. In fact, the hydrolysis is a complex process involving, apart from the hydrolysis reactions, parallel polymerization reactions which result in a great variety of polynuclear species [4]. The nature and extent of polymerization is not yet fully understood, and the efforts for explaining this phenomenon are based on specific products, which have been experimentally determined, and on observations from potentiometric titrations. Jia et al. [5] proposed a simplified scheme (Fig. 2) about the possible hydrolysis and reaction pathways of aluminium. The reactions 1-4 represent the hydrolysis products of  $Al^{3+}$  with increasing pH values, produced relatively quickly. The other reactions refer to possible polymerization reactions that lead to the formation of larger polymeric structures, which require more time to be formed, while the extent of their formation is not clear.

Among the possible products, the dimer ( $Al_2(OH)_2^{4+}$ ), trimer ( $Al_3(OH)_4^{5+}$ ), tridecamer ( $Al_{13} - AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{6,7+}$ ) and more recently  $Al_{30}(Al_{30}O_8(OH)_{56}(H_2O)_{24}^{18+}$ ) have been determined through  $^{27}Al$ -NMR and X-Ray Diffraction studies [6,7]. It is suggested that a polynuclear species with up to 54 Al atoms ( $Al_{54}(OH)_{144}^{18+}$ ) can be also formed [4]. The most important reaction is regarded to be the one leading to  $Al(OH)_4^-$  formation (reaction 4), because this aluminium anionic form is claimed to be the precursor for the polymeric  $Al_{13}$  creation [8].  $Al_{13}$  with Keggin-like structure is claimed to be the most stable aluminium species in a partially neutralized Al-solution [7] and the improved coagulation properties of PAC are thought to be due to its existence, i.e. increased charge neutralization capability (coagulation) and increased molecular size and aggregation ability (flocculation). Moreover, the decrease of monomeric Al in favor of  $Al_{13}$  and of the other polymeric compounds eliminates the

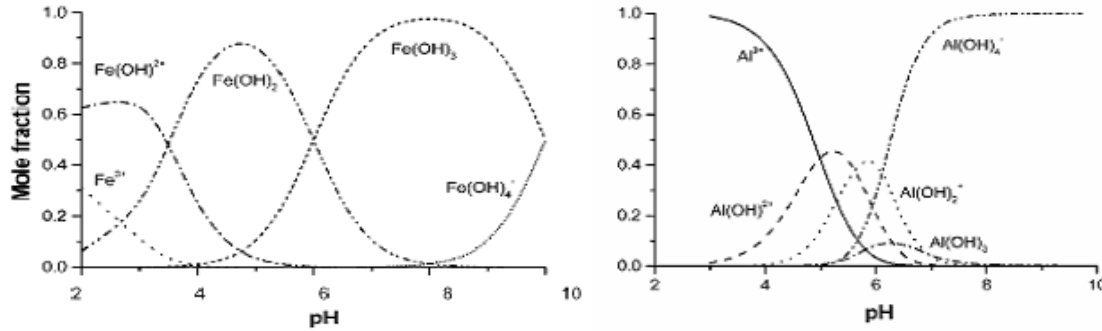


Fig. 1. Effect of pH variation in Al(III) and Fe(III) species distribution.

hydrolysis reactions and therefore, results in a minor impact of the pH value after treatment.

Similarly, the Fe(III) hydrolysis products are considered to be the following: five type of monomers ( $\text{Fe}^{3+}$ ,  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Fe}(\text{OH})_3$  (molecule),  $\text{Fe}(\text{OH})_4^-$ ), a dimer ( $\text{Fe}_2(\text{OH})_2^{4+}$ ), a trimer  $\text{Fe}_3(\text{OH})_3^{5+}$ , and a solid precipitate  $\text{Fe}(\text{OH})_3$ . Additionally, there also a wide range of dissolved polymeric species Fe(III) species with medium and high molecular weight. These polymeric species may well be described by the following general formulations:  $\text{Fe}_x(\text{OH})_y^{(3x-y)+}$ , or  $[\text{Fe}_x\text{O}_y(\text{OH})_{x+r}]^{(2x-2y-r)+}$  [2,3].

## 2.2 Properties of IPFs

Concerning the conventional coagulants, the aforementioned reactions cannot be controlled, and the coagulation efficiency is based more on the formation of  $\text{M}(\text{OH})_3$  and less on the charge neutralization, as the hydrolysis reactions are proceeding fast and hence, the concentration of positively charged Al/Fe ions is restricted. Furthermore, the performance of simple Al and Fe salts is sensitive to changes in the nature of the sample, e.g. temperature, pH, concentration of colloids and suspended particles. In the case of IPFs, the pre-polymerization aims to control, up to a certain extend, these reactions, resulting in products containing pre-formed polymerized species. Such species are resistant to further hydrolysis and consequently, they possess superior coagulation properties when used in water treatment.

In laboratory scale, the preparation of IPFs involves the partially neutralization of a dilute aluminium/iron solution (e.g.  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ) by a base solution (e.g.  $\text{NaOH}$ ,  $\text{NaCO}_3$ ) under high shear mixing conditions, resulting in rather diluted solutions. For commercial purposes and industrial applications, dense and stable solutions are required. The preparation in full scale is more

complicated and, generally in the case of aluminium, involves the production of two solutions that contain Al [9], i.e. the basic aluminium chloride and sodium aluminate. These are produced through processing an aluminium containing raw material ( $\text{Al}_2\text{O}_3$ , bauxite) under vigorous conditions (e.g. high temperature, pressure, extended contact time) with concentrated acid (e.g.  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ , or a mixture of them), or with a strong alkaline solution (e.g.  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{KOH}$  etc.). Through mixing under stirring of these solutions, a product is formed, which is characterized as polyaluminium chloride (PAC or PACl), when  $\text{HCl}$  is used and can be described with the generic formula  $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$ , where  $0 < m < 3n$ . A process for commercially preparing polyferric sulphate coagulant has been proposed [10]. According to this method, acidic solution of ferrous sulphate is oxidized to form ferric sulphate in an oxidation stage at ambient pressure and relatively high temperature ( $90^\circ\text{C}$ ) and in the absence of oxidation catalyst, using an oxidizing agent, preferably nitric acid. Then, the ferric sulphate is partially neutralised by the addition of sodium bicarbonate solution. The ferric sulphate is kept in contact with the base at the temperature selected (i.e.  $50^\circ\text{C}$ ) for a time sufficient for polymerization of the hydrolyzed ferric sulphate, notably 3-5 hours. The PFS structure can be described by the simplified formula  $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{(3-n/2)}]_m$ , where  $m$  is a function of  $n$  and  $n = 2y/x$  with  $n \leq 2$ .

The nature and composition of the final product varies according to the preparation method and the starting materials used. The preparation parameters that affect the distribution of the metal species include the temperature, the base addition rate, the mixing rate, aging time, presence of other anions (e.g.  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ) and the concentration of Al(III) or Fe(III) ions. The most important factor, however, is claimed to be the molar ratio of bound

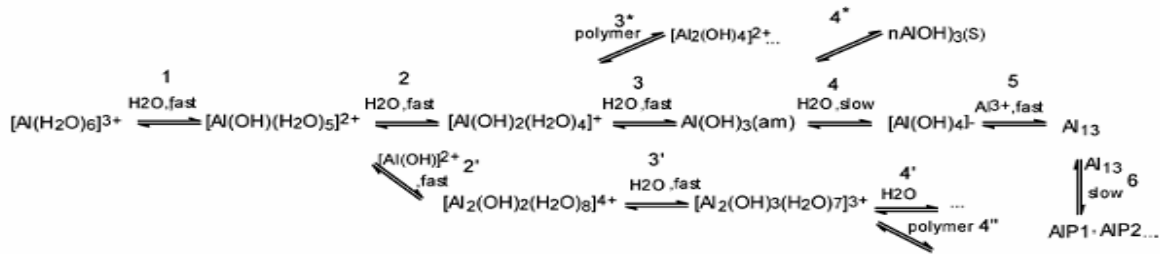


Fig. 2. Hydrolysis and possible polymerization reactions of aluminium

hydroxide to the concentration of metal ions regarding the total metal hydrolysis products, i.e.  $[OH]/[M]$  (or  $m/n$ ) and is used to describe the polymerization degree of coagulants that are prepared mainly in laboratory scale. Usually it takes values from 0.5 to 2.5 and 0.25-1.5 for aluminium and iron products respectively, as for values higher than 2.5 or 1.5 it has been observed that the solutions are unstable and precipitation occurs. In the case of aluminium commercial products, the term basicity is more common, representing the degree at which the hydrogen ions produced by hydrolysis of the metal ions are pre-neutralized [1].

$$\text{Basicity (\%)} = \left( \frac{[OH]}{[M] z} \right) * 100$$

where  $z$  corresponds to the charge on metal species (for Al,  $z=3$ ). The influence of all the above mentioned parameters has been extensively examined during the last 25 years [11-14].

Various pre-polymerized reagents are commercially available and are referred as polyaluminium chlorides (PAC), polyaluminium sulfates (PAS), or polyaluminium chloro-sulfates (PACS) and polyferric chloride (PFC), polyferric sulfate (PFS) for Al and Fe respectively, depending on the raw materials used. These products are available in solid or liquid form with variable degrees of polymerization and metal content. In particular, according to the American Water Works Association (AWWA), the main characteristics of a PAC solution should be: aluminium content 2.5-13 %w/w and basicity 10-83 [15].

### 3. Improved Inorganic Pre-polymerized Flocculants

The coagulation efficiency of the inorganic polymeric flocculants is significantly higher than that of the respective non-polymerized coagulants, but still it is much lower than that of the organic polymeric coagulants (OPC). The basic prerequisites for an effective coagulant are the charge-neutralisation capacity and the bridge-

aggregation ability. There are two ways for improving the efficiency of the IPFs; either by increasing the proportion of the polymeric species in their original composition or by adding other components to produce new composite coagulants. Additionally, the selected modifiers may also act as inhibitors to the precipitation of iron and aluminium, thereby improving the stability of the coagulants, which is a common problem. Wang and Tang [16] suggested three types of compounds that may be employed as modifiers: a) inorganic anions, such as polysilicates, phosphates, b) organic anions, such as various organic acids, and c) organic polyelectrolytes either cationic, non-anionic or anionic [16, 17].

#### 3.1 Increase of the effective metal species content

The superior performance of pre-polymerized coagulants is strongly related to certain polymerized metal species. In laboratory scale, the pre-polymerized chemicals produced can get a very high degree of polymerization, i.e. in the case of PAC very high content of Al<sub>13</sub> (up to 90%). In industrial scale, however, despite the achievement of high basicity values (up to 80%), the greater content of metals inhibits the Al<sub>13</sub> formation, as it is more possible that the formed Al<sub>13</sub> species aggregate to form bigger molecules. At present, the commercial PAC solutions contain relative low content of Al<sub>13</sub> (<50%), and there are still some limitations for other preparation methods to increase the Al<sub>13</sub> content at high basicity. Several efforts have been made to establish an alternative preparation method which will increase the content of the effective aluminium species. Particularly, the synthesis of PAC by utilizing a membrane reactor was proposed [5]. The principle is that by using an UF membrane through which the base is added to Al solution, the reduction of the size of the permeating drops results in the decrement of local supersaturation and consequently in the decrease of precipitates formation and the increase of the Al<sub>13</sub> content. Alternatively, electrochemical processes

were also adopted [18], resulting in PAC solutions with higher content of the active specie  $Al_{13}$ .

Chen and Yu [19] proposed a microwave assisted preparation of Polyferric Sulphate. According to this method, a reduced proportion of an oxidant and catalyst is required by applying the high pressure and high temperature characteristics of microwave radiation. The authors suggest that the microwave-prepared PFS has a better coagulation performance than the conventional PFS; however, there are no measurements concerning the polymerization yield.

The aforementioned techniques were applied only in laboratory scale experiments and have not been evaluated using higher (commercial grade) Al or Fe content. Further more, their influence on the performance of 'refined' prepared solutions is questionable, as no relevant coagulation experiments exist in the literature.

### 3.2 Modified IPFs based on silica addition

The main reason for the higher efficiency of organic polymers than the IPFs, is their higher molecular weight, which implies better flocculation properties. It is suggested that this advantage of OPCs can be compensated with the addition of selected components in the IPFs to produce new composite coagulants. By the appropriate introduction of these components and their subsequent polymerization, an increase of the molecular weight of the coagulants ingredients is expected, resulting in enhanced aggregating power and bigger and denser flocs formation.

Several research efforts have been made during the past few years, by using as additive polysilicates for achieving the incorporation of silica chains in the coagulants structure [20]. Hasegawa et al. [20] reported that by the introduction of metal ions into the polysilicic acid solution, the molecular weight of the coagulant increases and the coagulation efficiency as well as the stability of the products improves. In this case, the new coagulant is described as an inorganic metal-polysilicate coagulant, where polysilicates are the main component. More recently, research has focused on the incorporation of silica within the pre-polymerised metal solutions, which can be accomplished by two methods; either by introducing polysilicates in the pre-polymerised metal solution, or by adding polysilicates in the metal solution, followed then by the metal polymerization. The former method is referred as composite polymerization, while the latter as co-polymerization.

Polysilicic acid, which carries negative charge, consists of silica tetrahedrons, which are linked through silicon-oxygen-silicon bonds. The polymerisation of silicic acid will produce a wide range of silica species, including dimeric ( $Si_2O_3(OH)_4^{2-}$ ), trimeric ( $Si_3O_5(OH)_5^{3-}$ ), tetrameric ( $Si_4O_8(OH)_4^{4-}$ ) and eventually polymeric species [21]. The rate of silicic acid polymerization is strongly pH-dependent; being very fast in neutral and slightly alkaline solutions and very slow at low pH values (2-3).

Several authors have reported the production and study of polyferric silicate coagulant in laboratory scale [16, 22]. Major attention has been paid to certain parameters, i.e. Fe/Si, OH/Fe molar ratio, pH and additionally, to their effect upon the properties of the coagulants. It is suggested that the Fe/Si and OH/Fe molar ratio affect the polymerization yield, the species distribution, the z-potential and as far as the OH/Fe ratio is concerned, the stability of the products [16, 22]. Additionally, the relation between z-potential and pH and Fe/Si has been investigated, illustrating that the addition of polysilicic acid compromises the charge neutralization ability of the pre-polymerized coagulants, due to the fact that (partial) charge neutralization occurs, when hydrolyzed ferric species of different charge are combined with polysilicic acid [22].

In the case of aluminium, the new composite coagulants are characterized as polyaluminium silicate chlorides (PASiC). The parameters that affect the nature of the final product are the same as for polyaluminium solutions, including the molar ratio of aluminium to silica content (Al/Si ratio) and the preparation technique applied. Through studies examining the chemical species distribution in these new products, it was revealed that the incorporation of silica in the structure of polymerized metal solutions resulted in the decrease of  $Al_{13}$  content [13, 23, 24] and the reduction in the charge neutralization capability of coagulants [25], as compared to the respective PAC solutions. Despite these negative effects in the nature and composition of the silica-based coagulants, the increase of colloids/particle size of these coagulants seems to be important [26], as it results in the enhancement of the aggregation ability and consequently, in more effective coagulation performance.

Regarding the new modified coagulants with iron, no references concerning their commercial status have been found and no preparation methods in industrial scale were located.

Table 1. Comparison of coagulation \* performance of Al-based coagulants

Coagulant	Turbidity removal (%)			Absorbance at 254 nm removal (%)			Residual Al concentration ( $\mu\text{g/L}$ )		
	pH value of treated sample			pH value of treated sample			pH value of treated sample		
	7	8	9	7	8	9	7	8	9
<b>Alum</b>	85.8	79.0	72.0	69.0	62.1	56.9	400	590	684
<b>PAC-18</b>	92.4	90.5	86.0	78.4	69.8	67.2	243	459	632
<b>PAC<sub>lab</sub></b>	93.0	91.8	88.5	82.8	78.0	73.7	177	180	294
<b>PASiC</b>	92.7	92.0	88.2	84.1	79.7	72.4	132	170	232

\* Initial turbidity 16 NTU, initial absorbance at 254nm 0.125, dose of coagulants 2mg/L

Table 2. Comparison of coagulation \* performance of Fe-based coagulants

Coagulant	Turbidity removal (%)			Absorbance at 254 nm removal (%)			Residual Fe concentration (mg/L)		
	pH value of treated sample			pH value of treated sample			pH value of treated sample		
	5	7	9	5	7	9	5	7	9
<b>FS</b>	80	82	81	37	38	37	540	530	510
<b>PFS</b>	86	84	85	39	42	41	490	510	480
<b>PFSiS</b>	96	97	97	78	66	61	430	400	340

\* Initial turbidity 10 NTU, initial absorbance at 254nm 0.120, dose of coagulants 4mg/L

For aluminium coagulants, preparation methods (industrial purposes) for some modified products have appeared in the literature, e.g. for the production of polyaluminium silicate sulfate with relative low content of silica (Al/Si molar ratio 20) [27].

#### 4. Comparison of coagulation performance

The IPFs exhibit a superior coagulation performance compared with the conventional non-polymerized ones. Their advantages are attributed to: (a) high concentration of polymeric species, (b) wider working pH range, (c) lower sensitivity to low water temperature, (d) lower dose requirements for achieving equivalent performance with the conventional coagulants, (e) lower residual metal-ion concentration, and (f) lower sludge production. In particular, it is reported that pre-polymerized coagulants (PAC, PFS, PFC) have a superior efficiency in the removal of NOM, turbidity and colour, as well as of algal-derived organic matter, than the conventional coagulants [3, 28]. Similarly, some studies have shown that the silica-based modified IPFs also exhibit satisfactory coagulation efficiency and in some cases they are superior than the non-modified [16, 26, 29-32].

An example of the comparative performance of polyaluminium silicate chloride (PASiC with OH/Al=2, Al/Si=10) in comparison with laboratory prepared polyaluminium chloride (PAC<sub>lab</sub>) with relatively high degree of polymerization (OH/Al=2), a commercially available product

(PAC-18) with relatively low degree of polymerization (OH/Al=1.2) and aluminium sulphate (alum) for treating kaolin-humic acid model suspension is presented in Table 1. Similarly, Table 2 illustrates the comparative results of Polyferric Silicate Sulphate (PFSiS, OH/Fe=0.5, Fe/Si=1.0, polymerization degree 38%), polyferric Sulphate (PFS, OH/Fe=0.3, pol. degree 35%) Ferric Sulphate (FS, non-polymerized). These results were obtained the respective laboratory-scale experiments.

Table 1 shows that the least effective coagulant is alum (non-polymerized) in all cases. Regarding the pre-polymerized aluminium coagulants, the increase of polymerization degree results in an improvement in coagulation performance, as PAC<sub>lab</sub> is more efficient than PAC18. PASiC with the same degree of polymerization with PAC<sub>lab</sub> exhibits almost equal performance in turbidity and absorbance at 254 nm reduction with PAC<sub>lab</sub>. The relevant advantage in the use of the silica-based coagulants can be concluded from the lower residual aluminium concentration. The differences are quite large, when compared to the coagulants with none or lower polymerization degree, as alum or PAC-18. PASiC seems to create significantly less residual aluminium concentration, especially at the higher (alkaline) pH region, whereas alum and PAC-18 seem to be less appropriate for use, because of the respective higher residual aluminium concentration. In the pH range 7-9, i.e. the usual pH range of natural waters, the aluminium concentration remains under or close to 200  $\mu\text{g/L}$  (EU maximum permissible concentration limit of Al for drinking water [33]).

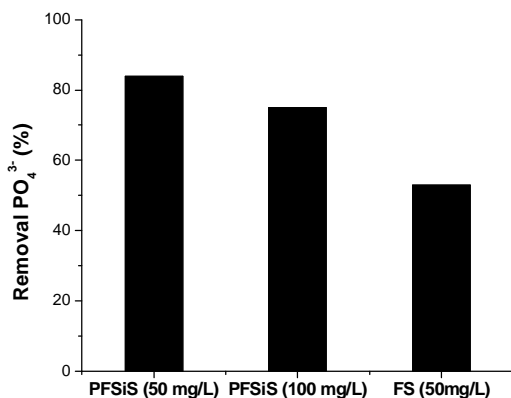


Fig.3. Removal of  $\text{PO}_4^{3-}$  ions from a biologically pre-treated leachate by the addition of Fe-based coagulants.

Moreover, PASiC seems to be even better than the laboratory prepared PAC, indicating the importance of aluminosilicate complexes formation. It is suggested that the presence of silica enhances further the resistance of aluminium species to hydrolysis [26].

Similarly, the data of Table 2 illustrates that the most efficient coagulant is the modified coagulant (PFSiS) in terms of removing both turbidity and NOM (expressed as UV absorbance) compared with the pre-polymerized (PFS) and the non-polymerized (FS) coagulant, which is attributed to the presence of silica, as the difference in the polymerization degree is not that high comparing with PFS. It is worth noting that both PFS and PFSiS coagulants exhibits similar performance in all 3 pH values (slight acidic, neutral, slight alkaline) of the treated sample, indicating that they equally perform in a wider working pH range. Additionally, the advantage in using the silica-based coagulant is illustrated by the lower residual iron concentration in the treated water. It is evident that the residual concentration is consistently lower than the samples treated with PFS and FS irrespective of the pH value of treated sample, as the presence of silicates compromises the tendency of iron for further hydrolysis. In addition to this, the modified coagulant PFSiS exhibits a very good coagulation performance when treating wastewater mainly for the removal of phosphate ions. Fig.3 illustrates the comparative results of the removal of  $\text{PO}_4^{3-}$  ions when biologically pre-treated leachate is treated by Fe-based coagulants. It is evident that the PFSiS exhibits a superior coagulation performance than the FS, achieving a removal of

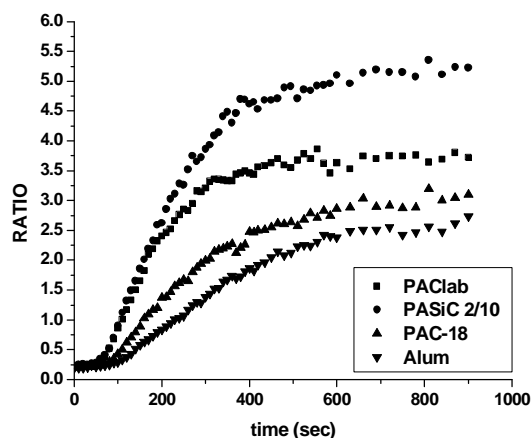


Fig.4. Kinetics of coagulation of the Al-based coagulants

$\text{PO}_4^{3-}$  up to 84% (i.e.  $0.57 \text{ mg/L PO}_4^{3-}$ ), hence  $<1 \text{ mg/L}$ , which is the limit concentration value in wastewaters to be discharged in sensitive to eutrophication surface waters, according to the respective legislation [34].

Moreover, the extent of aggregation, as well as the kinetics of coagulation of the Al-based coagulants has been examined with the aid of Photometric Dispersion Analyzer (PDA). In particular, Fig. 4 [26] illustrates the flocs growth during the coagulation of the kaolin-humic acid model suspension with Al-based coagulants. It is clear that with all pre-polymerized reagents the duration of flocs growth period is limited (shorter duration of lag phase) compared to alum.

From the Ratio values it can be concluded that the aggregation ability is higher, as Ratio values increase with increasing size of flocs [31]. With higher polymerization degree the increment of floc size is greater, and the addition of silica (PASIc) further enhances this increment, resulting in bigger and denser flocs formation.

## 5. Future trends

The preparation and properties of silica-based modified IPFs are still under investigation. At the same time, alternative additives are considered that they would have a more significant effect on the improvement of IPFs properties.

In many water treatment facilities the combination of inorganic coagulants and organic polyelectrolytes in separate steps for the enhancement of flocculation is a very common procedure. It is suggested that combining these reagents into one, a superior coagulant could be

produced, with the additionally benefits of cost and time saving. Particularly, by the introduction of a cationic polyelectrolyte into the structure of a pre-polymerized metal coagulant, the charge neutralization capability as well as the aggregating effect is expected to improve. Moreover, the usage of an anionic polyelectrolyte with higher molecular weight (compared to cationic) would further improve the aggregating ability. In this case, however, the anionic polymer should have weak anionic charge, in order not to deteriorate, up to a high extent the charge neutralization strength of the combined coagulant. Some efforts have been reported regarding the combination of PAC with various anionic, cationic and non-ionic organic polymers [17] and the combination of PAC or PFC with poly-dimethyl-diallyl-ammonium chloride (PMDAAC) [35, 36] and promising results were obtained regarding their coagulation performance. Additionally, combination of aluminium and iron in the structure of a pre-polymerized coagulant has also been proposed [37], while it is also suggested that addition of silicates in such a mixed coagulant results in the production of a more complex poly-aluminium-ferric-silicate-chloride [25].

It can be concluded that the tendency in the coagulation field nowadays is the production of modified composite coagulants, which they are becoming more and more complicated, regarding their composition. The variety of the possible additives and the different possible mixing ratios of them state clearly that the concept of "mixing" to produce superior chemicals is in an initial stage and more research efforts can be devoted to this purpose.

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